

# STRUCTURE OF SURFACES AND INTERFACES

## Liquid Surface Studies

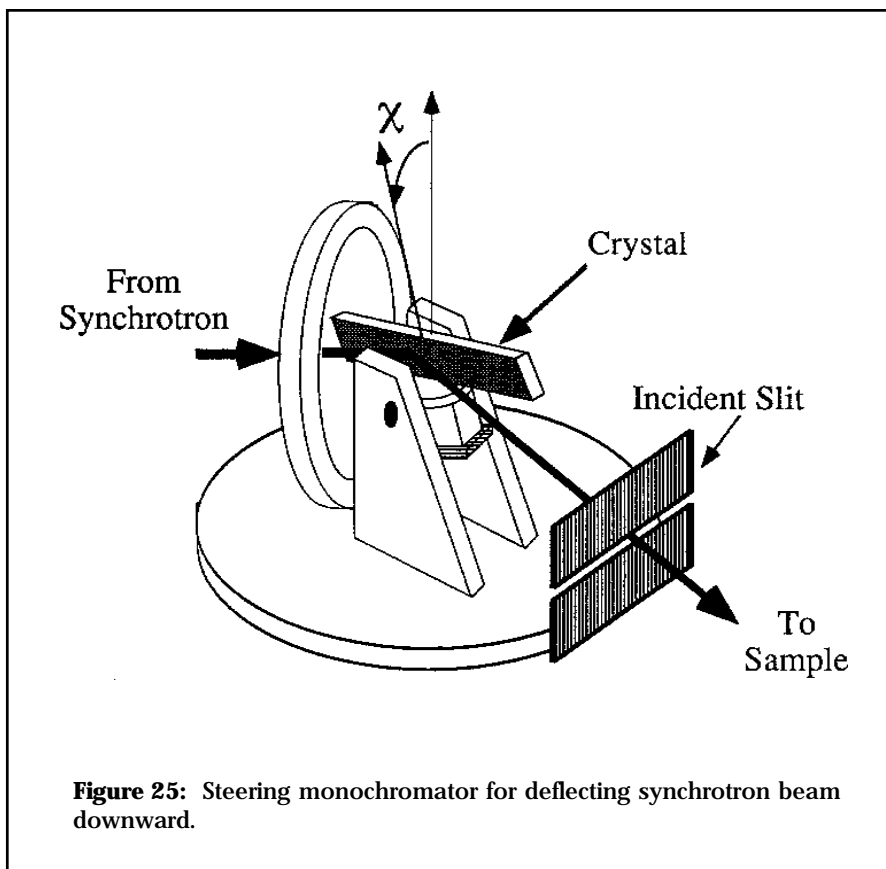
Liquid interfaces are relevant to many disciplines, including biology, physics, and chemistry, yet relatively little is known about the structure of these interfaces. For example, the physical interactions that stabilize the liquid/vapor interface and give rise to surface tension can also give rise to interfacial structure which is very different from that found in the underlying bulk. Scattering experiments that make use of the high brilliance of x-ray synchrotron sources are one of the few experimental methods - compared to those available at solid interfaces - which are capable of investigating the microscopic structure of liquid interfaces. Over the last decade a wide variety of liquid surfaces and interfaces have been studied at NSLS including liquid crystals, simple dielectric liquids, liquid metals, molten chain molecules and organic monolayers on both water and liquid metal subphases. Many of these studies were scientific "firsts", and revealed new phenomena and novel features for the corresponding surfaces. Some of the more important scientific results obtained at the NSLS are the quantitative confirmation of long-standing theoretical predictions of the capillary contribution to the surface roughness in water, ethanol, alkanes, and liquid metals, the roughness and surface correlations of a surfactant monolayer at an oil-water interface in equilibrium with a microemulsion, the microscopic structural relaxation of condensed Langmuir monolayer phases of fatty acids and esters, the nature of the layering transition at the surface of isotropic phase of a liquid crystal, the adsorption at, and structure of polymers at liquid surfaces, surface crystallization at temperatures above the bulk melting point in normal alkanes and alcohols. In addition, measurements resulted in the first unambiguous proof of the long standing theoretical predictions of surface induced atomic layering along the surface normal of liquid Hg, Ga and In. The surface induced layering in Ga-In and Ga-Bi alloys and

the in-plane structure of the solute-rich surface layers of dilute Bi-Ga and Sn-Ga alloys, and the oxide formation on liquid Ga, were also studied recently, and provided important insights into fundamental issues of surface segregation and surface oxidation, respectively.

This broad spectrum of liquid surface studies at NSLS helped to provide an essential basis for obtaining a microscopic understanding of liquid interfaces in general. In this short overview, we will concentrate only on the more recent findings at NSLS concerning liquid surfaces. Earlier results are well documented in the literature.

## Experimental

Spectrometers for studying liquid surfaces are fundamentally different from standard four-circle diffractometers. The free liquid surface is always horizontal, and thus the horizontal beam originating at the ring has to be deflected downward to impinge on the surface at a given angle. This is usually accomplished by tilting a crystal in the Bragg geometry downward as shown in **Figure 25**. Specialized instruments employing this method have been employed at X19C, X20, X22B, and X25. This



**Figure 25:** Steering monochromator for deflecting synchrotron beam downward.

requires precise control of the vertical positions of the sample, beam defining slits and detector. General purpose liquid spectrometers employing this method are capable of studying the structure within the plane of the surface (by grazing incidence x-ray diffraction, GIXD) as well as along the surface normal direction (by x-ray reflectivity, XR). While downward deflection of the beam can also be done using an x-ray mirror, and was implemented in some liquid metal experiments on X10A, this geometry is suitable for GIXD only and can not accommodate reflectivity measurements.

Environmental chambers for liquid surface measurements depend on the nature of the surfaces studied, and range from sophisticated UHV chambers (for studies of highly reactive liquid metal surfaces, for example) equipped with residual gas analyzers and ion beam sputtering guns for cleaning the sample's surface, through Langmuir troughs (for studying monolayers of amphiphiles and polymers on water) equipped with moveable barriers for *in situ* monolayer compression and Wilhelmy plate balances of surface tension monitoring, to small and simple temperature controlled sealed cells (e.g. for studying surface crystallization of alkanes). A detailed description of these cells is beyond the scope of this brief review, and can be found in the literature. Selected examples follow:

### **Liquid Metals**

An important prediction, central to the theoretical understanding of the structure of liquid metals is that of atomic layering at the surface. According to this prediction, atoms near the surface will be ordered in layers parallel to the surface, and the layering amplitude should decay with depth below the surface with a characteristic length of several atomic diameters. Although over two decades old this prediction was hitherto untested experimentally in spite of substantial efforts by several groups worldwide. In a series of experiments by a group from Bar-Ilan, Harvard and the Brookhaven Physics Department (BHB) at X22B and X25 this effect has been confirmed for both liquid mercury and gallium. The surface layering gives rise to a broad quasi-Bragg peak in the x-ray reflectivity spectrum at a momentum transfer  $q_z \approx 2.2\text{--}2.5 \text{ \AA}^{-1}$  corresponding to the layer spacing  $d = 2\pi/q_z \approx 2.5\text{--}2.8 \text{ \AA}$ , which is close to the value for the atomic diameter of the metal. The layering is an intrinsic, and highly persistent, property of liquid metals, as indicated by the nearly identical layering observed for bare and self-assembled thiol monolayer covered mercury surface. The studies of the Hg and Ga surface have been extended to cover a wide temperature range, and also to various alloys.

In addition, the effects that varying oxygen exposure has on the surface of liquid Ga have also been studied at room and elevated temperatures. The formidable challenge to all of measurements on liquid metals is the need to measure over a large dynamic range in both  $q_z$  and reflected intensity while maintaining an oxide-free surface for samples almost all of which are highly reactive.

In the case of binary liquid metal alloys, surface segregation of one of the components often reduces the interfacial energy, e.g. the surface tension, and even for very dilute alloys, the surface may have a very different composition than that of the underlying bulk alloy. Studies by Ning Lei, and colleagues at X19C have investigated the structure of gallium alloys with bismuth and tin. In the case of the bismuth alloy, grazing angle diffraction studies indicate that the bismuth segregates into a nearly complete monolayer atop the bulk alloy where the bismuth monolayer has the structure of a supercooled liquid. The surface tension of the alloy is obtained by interpretation of measurements of the diffuse scattering around the specular axis in terms of thermally excited capillary waves. From reflectivity measurements of the gallium-tin alloy, it is found that the tin concentration at the surface is in excess of the bulk concentration and that it decreases with increasing temperature, in accord with the Gibbs isotherm. X-ray reflectivity measurements of the gallium-indium alloy at X25 by the BHB group leads to a surface layer with a much higher electron density than the underlying liquid. Model fits assign this to single indium layer, with subsequent layers at the bulk eutectic composition. Ga oxidation studies by the same group show that on exposure to  $\sim 180$  Langmuirs of oxygen, a thin layer of gallium oxide forms at the liquid Ga surface. As shown in **Figure 26 (see next page)** this leads to modulations in the reflectivity profiles which are well described by a uniform 5 Å thick oxide layer. The reflectivity does not change for exposures up to 1600 Langmuir, nor for elevated temperatures up to 300°C, indicating that the oxide layer is solid. The oxide layer is, however, most probably amorphous, since first GIXD measurements failed to show any dpeaks. Finally, the previous x-ray reflectivity measurements on Hg by the BHB group have been extended at X22B down to temperatures just above the melting point, -38.9°C. Here it is found that the peak in the reflectivity (associated with surface layering) increases dramatically in intensity with decreasing temperature with no corresponding change in the peak width. The latter result demonstrates that the intrinsic local decay of the stratified density profile is independent of temperature, consistent with similar results obtained for the Ga surface.

## Langmuir Monolayers

Studies of organic molecules adsorbed on the surface of water, Langmuir monolayers, continue to be one of the more active areas of investigation. Ever since 1917, when Langmuir first developed what subsequently became known as the Langmuir film balance, surfactant or Langmuir monolayers (LM) have been extensively studied using a variety of techniques. It is only recently that the availability of synchrotron radiation sources has allowed grazing incidence diffraction to be used to learn the microscopic, molecular structure of these films. Part of the reason for the broad current interest in LM is that they are one of the few realizable systems in which a film exhibiting two dimensional (2D) statistical physics can be tuned in a manageable way by varying the molecular structure. As a result, the phase diagrams of LM are enriched in comparison with those of simpler monatomic systems. In addition, many of the properties of LM can be related to those of biological membranes and to thin organic films that are used for lubrication and other

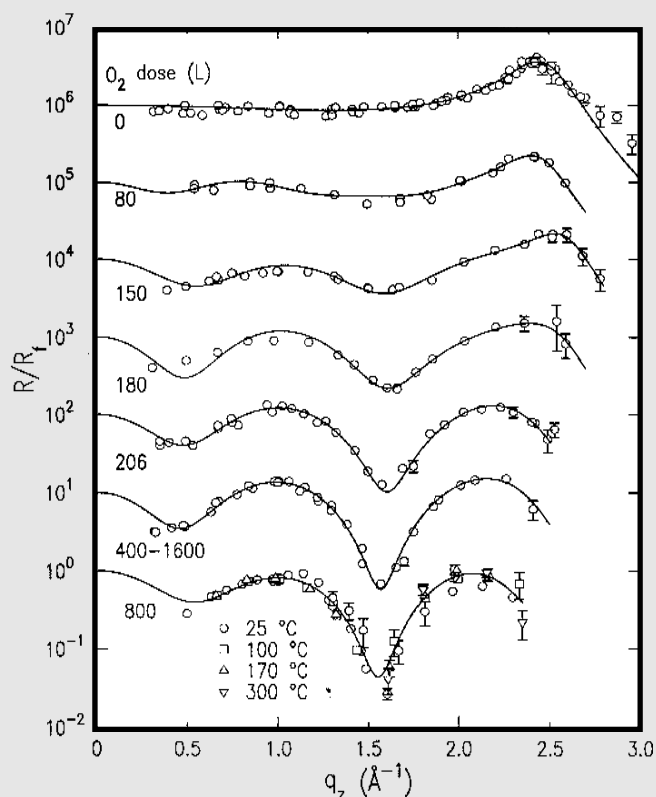
purposes. Although initial investigations were carried out on simple soap like molecules which contain a hydrophobic tail and a hydrophilic headgroup, increasingly more complex molecular architectures were investigated over the last few years and recent studies addressed such systems as fullerene derivatives, gold colloids, discotic and nematic liquid crystalline materials and water-soluble pigments at lipid interfaces.

One unfortunate aspect associated with application of the GIXD technique to probe the structure of 2D phases of LM is the fact that the scattering cross section for most of the surfactants that have been studied is not sufficient to observe the structure factor of phases with the short positional correlation lengths that are typical of liquid phases. One exception to this is the study by a group from Harvard and Ames Laboratory, at X22B, in which they measured the structure factor of an amorphous phase of a LM of a fullerene-propylamine adduct ( $C_{60}$ -PA), consisting of a  $C_{60}$  molecule and twelve propylamine ( $NH_2(CH_2)_2CH_3$ ) chains attached to it.

This molecule is sufficiently large that the structure factor of the LM could readily be separated from the diffuse background scattering from the ambient He gas above the monolayer and the bulk liquid water below.

**Figure 27** illustrates GID scans (with background subtracted) for LM of  $C_{60}$ -PA at different surface densities. When the effect of the calculated molecular form factor is included the peak position at  $\sim 0.42 \text{ \AA}^{-1}$  corresponds to the average nearest neighbor distance of  $\sim 13.2 \text{ \AA}$  which is close to the diameter of the molecule and corresponds to a molecular area of  $\sim 151 \text{ \AA}^2/\text{mol}$ . This is very close to the specific area at which the surface pressure increases (inset to **Figure 27**). Although this LM was an amorphous solid, the hope is that if LM systems can be developed in which the fullerenes phase will be fluid it would be possible to study 2D melting/solidification. A second system in which GIXD studies of a disordered phase reveal the broad peak associated with a system having only short range order is gold colloid monolayers, studied by Clarke and collaborators at X22B. In addition to GIXD studies x-ray reflectivity measurements indicate a monolayer to bilayer transition with increasing 2D density.

Studies of LM systems with smaller molecules, for which the in-plane order was only observed for phases with relatively long range order include the discotic liquid



**Figure 26:** Fresnel-normalized reflectivity from the surface of liquid gallium vs.  $O_2$  dosage and for different temperatures. (X25)

crystalline monolayers studied by a group from U. Penn at X22B. They studied LM of two different molecules, of which only one showed a single GIXD peak. A group from Northwestern, working on X14A, carried out similar studies on a LM of an azobenzene containing molecule. Although Brewster angle microscope studies carried out prior to the synchrotron measurement indicated the existence of a phase transition from a low density fluid phase to a higher density solid phase, the GIXD measurements indicated that both phases have the same degree of positional order, implying correlation lengths from 100 Å to 300 Å in each phase.

The Ames Laboratory/BNL collaboration also carried out a GIXD and reflectivity study at X22B to determine the structure of charged water soluble pigments that are adsorbed by charged lipid monolayers at the air-water interface. The combination of pressure/area isotherms and x-ray measurements shows that when the LM is spread on micro-molar solutions of the pigments the LM order is substantially different from that of the LM spread on pure water.

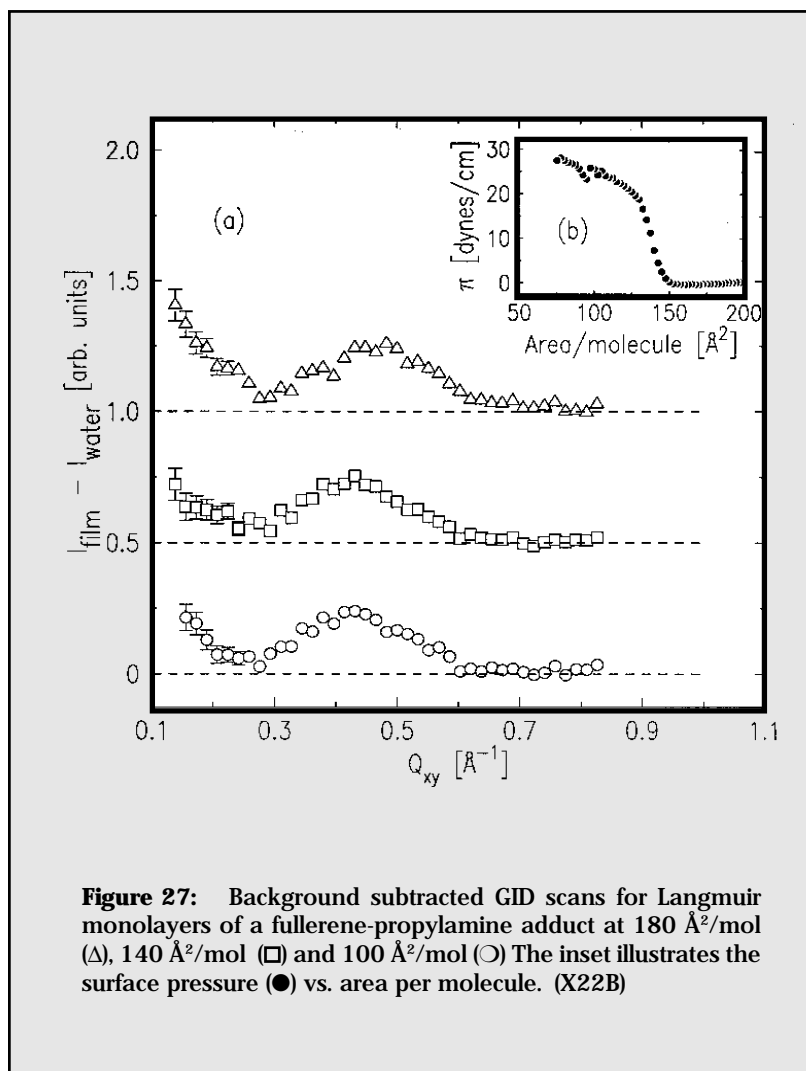
Finally the BHB group studied the formation of thiol mono- and multilayers on liquid mercury. This novel system is intermediate between Langmuir films on water and self-assembled organic layers on crystalline solids. It forms on a disordered liquid surface like the former, while its structure is dominated by the strong substrate-headgroup interaction like the latter. The monolayers formed were found to be well-defined and densely packed, with molecules aligned normal to the surface. Surprisingly, however, no long range in-plane order was observed for any of the chain lengths studied. The multilayers were found to have a complex bi-layer structure with Hg atoms intercalated in the center, and are well-ordered in-plane, with a highly oblique unit cell resembling that of bulk mercury thiolate.

### Surface Freezing

A group of researchers from Brookhaven, Exxon, Argonne and Bar-Ilan found in measurements carried out at NSLS a few years ago that normal-alkanes and alcohol exhibit surface freezing, i.e. a spontaneous formation of a solid layer at the surface of the melt at temperatures of a few degrees above the bulk melting temperature. This is a very rare

phenomenon, since almost all other materials show the opposite surface melting effect following a general Statistical Mechanics principle. X-ray measurements at X22B showed the surface-frozen layer to be a single monolayer in alkanes and single bilayer in alcohols. Their crystalline structure was fully characterized as a function of both chain length and temperature, resulting in a rich phase diagram including rotator and non-rotator phases of surface-normal and tilted molecules. More recent studies showed the same effect in alkane-alkane and alcohol-alcohol mixtures, which also exhibit a novel quasi-2D phase diagram for the surface layer, depending on the chain length difference of the components.

In related studies by the same group during this year, O. Gang (Bar-Ilan U.) and coworkers have shown that it is possible to tune the temperature range of existence as well as the surface layer structure of alcohols by judiciously chosen molecules added to the bulk at a few percent concentration level. Water molecules added to long chain alcohols were found to intercalate in between the two



**Figure 27:** Background subtracted GID scans for Langmuir monolayers of a fullerene-propylamine adduct at 180 Å<sup>2</sup>/mol (Δ), 140 Å<sup>2</sup>/mol (□) and 100 Å<sup>2</sup>/mol (○) The inset illustrates the surface pressure (●) vs. area per molecule. (X22B)

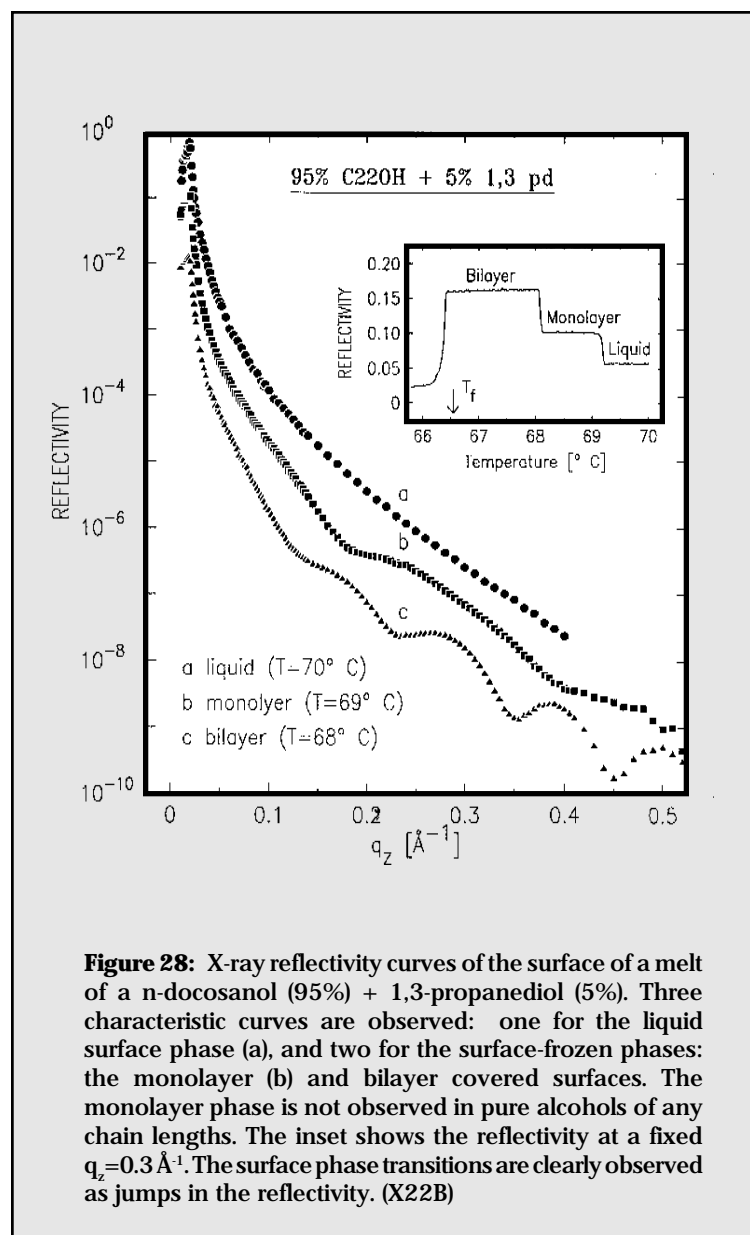
layers comprising the surface bilayer causing it to swell by  $\sim 2$  Å. In addition, the bilayer formation and bulk freezing temperatures are shifted up, and an increase of 1-2 °C is obtained in the range of existence of the bilayer. For longer chain alcohols, where tilted phases are observed, the intercalating water also reduces the molecular tilt by a few degrees, as compared to the dry pure alcohol. Another additive, a short a,w-diol, was found to induce a transition from a bilayer to a monolayer in the surface layer, which could be affected either through a concentration or a temperature variation. Reflectivities of the surface-frozen layer in the mono- and bilayer phases of the diol-laced  $C_{20}$  alcohol are shown in **Figure 28**, where their characteristically different shapes can be clearly observed. The monolayer phase seems to be stabilized by the adsorption of an

excess concentration of diol molecules at its lower surface, probably attracted by the layer of OH groups facing the melt. This demonstrates that “engineering” the structure of the surface phase by bulk additives is a viable, and exciting, possibility.

### Liquid-Liquid Interfaces

In addition to the liquid vapor interface, x-ray reflectivity studies have also been extended to the liquid-liquid interface. Following on the earlier work by McLain *et al.* (MIT), on the structure of the oil/water interface in equilibrium with a middle-phase microemulsion, M. Schlossman *et al.* (U. of Illinois @ Chicago), carried out a series of XR and GIXD studies on the oil/micremulsion interface of several ternary microemulsions containing a straight chain oil, water, and a surfactant from the homologous series  $C_iE_j$  (n-alkyl polyglycol ether  $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$ ). The main interest here is in the interplay between the non-monotonic interfacial profiles of the two liquids and the large amplitudes of the thermally-induced capillary waves, expected from the ultra-low,  $\sim 0.1$  mN/m, interfacial tension. The challenge for these measurements arises from the large absorption losses of the x-rays, which must traverse a long path inside the oil phase, as well as the very low reflectivity due to the high surface roughness. Schlossman's measurements used 15 keV x-rays and a sample cell  $\sim 35$  mm wide. Preliminary analysis indicates that the roughness of the surface of the mixture containing  $C_{10}E_4$  ( $s > 200$  Å) is considerably greater than that of mixtures containing either  $C_4E_1$  ( $s = 57$  Å) or  $C_6E_2$  ( $s = 45$  Å). All of these values are much larger than the corresponding molecular sizes, and indicate strongly fluctuating interfaces, as expected. Preliminary analysis of the measured diffuse scattering spectra yields a higher surface roughness than the reflectivity results, indicating the need for a more sophisticated approach than the step-function distorted wave Born approximation.

The application of synchrotron radiation to the structure of liquid surfaces is currently providing atomic level information that is not otherwise available. For LM as an example, GIXD measurements have revealed rich phase diagrams involving multiple two dimensional solid-solid phase transitions that correspond well with three-dimensional solid-solid phase transitions. Similarly XR measurements have confirmed the decades old predictions of the



layered structure of liquid metal surfaces and revealed new features that will continue to be the subject of future research for some years. Other technically challenging systems, like the liquid/liquid interface, will also continue to draw much attention, and will no doubt benefit from the high-energy mode of operation currently being explored at the NSLS as well as the higher brilliance and intensity available at present insertion-device sources at the NSLS.

## Solid Surfaces

X-ray diffraction continues to be an important experimental probe for the determination of the atomic structure of single-crystal surfaces, and the problems which are tackled by this technique grow successively more difficult. For example, the bulk crystal structure of gallium consists of dimers tilted slightly away from the (001) direction, and so it is interesting to know whether the surface simply truncates the bulk structure, or if there is a more complicated rearrangement. Preliminary results by D. Walko *et al.* (U. of Illinois), on X16A indicate that the surface is different from the bilayer self-wetted structure proposed theoretically. There has also been work on X22C to study whether Ir(001) becomes incommensurate, roughens, or disorders at high temperature, motivated by the behavior of Au and Pt. G. Watson *et al.* (U. of Maryland), found that it remains commensurate, and roughens above 2000 K. Under very different conditions, J. Wang and R. Adzic (Brookhaven National Laboratory) studied the (111) surface of Au in contact with a solid electrolyte. The experimental conditions guaranteed that the observed lifting of the reconstruction with electric potential was caused by the surface charge rather than by anion adsorption.

The addition of a monolayer film on a single crystal surface opens a rich variety of possibilities, and in-vacuum x-ray measurements are well-suited to their study.

P. Bennett *et al.* (Arizona State U.), made use of the high resolution intrinsic to x-ray scattering techniques to show that the monolayer Au on Si(001) 5x1 structure is actually incommensurate, in contrast to earlier LEED and STM results. A different technique, x-ray standing wave analysis, has been used to study the initial stages of adsorption of In on GaAs(001) and of Te on Si(001), (T.-L. Lee, *et al.*, Northwestern U. and P. Lyman, *et al.* LBNL), on X15A. It is also possible to prepare well-defined adsorbed phases from solution, and x-ray diffraction is particularly useful in penetrating the liquid overlayer to obtain atomic-scale information. L. Cheng *et al.* (Northwestern U.), used the x-ray standing wave technique to study the adsorption of selenite ( $\text{SeO}_3^{2-}$ ) ions on calcite. J. Wang *et al.* (Brookhaven National Laboratory), used beamline X22A to discover that mono- and bi-layers of electrochemically-deposited Ag form an incommensurate phase on Pt(111) which is compressed relative to bulk Ag. This is quite unexpected, because the reduced coordination at the surface usually leads to expanded surface layers. On the same beamline, B. Ocko *et al.* (Brookhaven National Laboratory), studied the ordering of Br on Ag(001), and observed Ising model critical behavior.

There were two interesting experiments on the formation of thin oxide surfaces in aqueous environments. A. Davenport *et al.* (Brookhaven National Laboratory), have studied thin oxide films on Fe(001) and (110) on beamline X20A. They find an epitaxial relationship between oxide and substrate. According to their results, the film is not one of the bulk forms of iron oxide, but rather is similar to the spinel  $\text{Fe}_3\text{O}_4$ , with a large fraction of oxygen vacancies and some displacement of the oxygen ions. In related work, Y. Chu and I. Robinson (U. of Illinois) have used X16C to study the oxidation of Cu(111) in perchloric acid. They find epitaxial cubic  $\text{Cu}_2\text{O}$  grows in two different orientations, in which one alignment grows to only a few monolayers, while the other can become significantly thicker.